Collision number, Collision Frequency, Collision Diameter, Mean Free Path, and Mean Free Time

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Questions

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Collision number, Collision Frequency, Collision Diameter, Mean Free Path, and Mean Free Time

Collision number

- At constant pressure and temperature,number of collision in a gas is called collision number.

Collision number Formula:

- Collision number is denoted by Z.

Collision number :

$$Z = \sqrt{2}\,\pi\sigma^2\bar{C}N'^2$$

where

π = mathematical expression

σ = Collision diameter

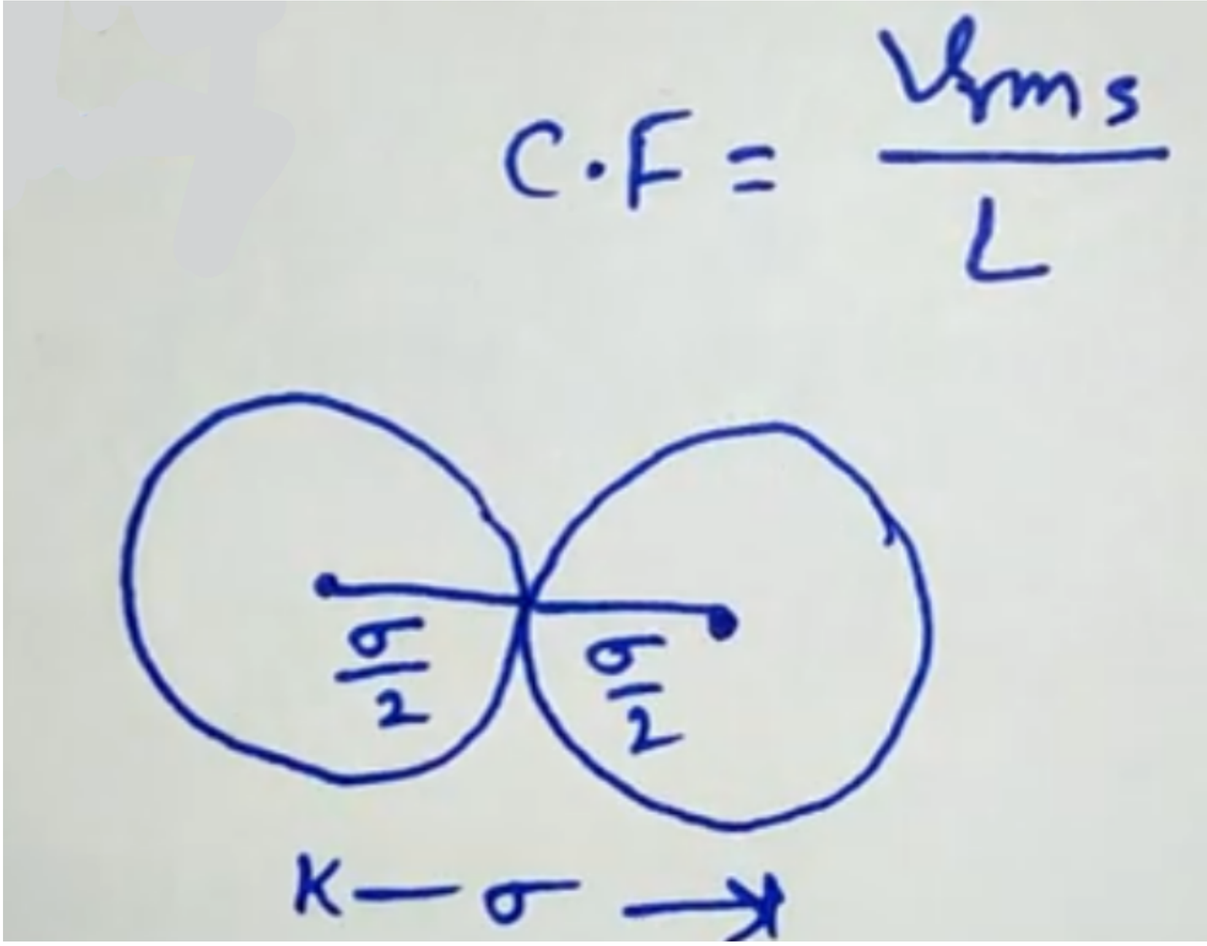
$\bar{c}$ = Average molecular velocity = $\sqrt{\frac{8RT}{\pi M}}$

N' = Number of gases particles per unit volume

Collision Frequency

⭐ Collision number is very high for a gas. So, we calculate collision number per unit volume and per unit time. This is called collision frequency.

- The number of collisions per second per unit volume of the reaction mixture is known as collision frequency.
- Collision frequency is an important parameter in the study of chemical kinetics and the calculation of reaction rates.
- The frequency of molecular collisions can be calculated from the mean free path and the average velocity.
- The Ratio of rms velocity and mean free path is known as collision frequency (C.F)


$C \cdot F = \frac{V_{rms}}{L}$
$\frac{\sigma}{2}$
$\frac{\sigma}{2}$
$\leftarrow \sigma \rightarrow$

Formula of collision frequency

- Collision frequency is denoted by Z_{11} for same type of molecule collide or Z_{12} for different molecules collide..
- The factor of (1/2) in the formula of collision number accounts for the fact that each collision is counted twice, once for each of the colliding particles.

Collision frequency :

$$Z_{11} = \frac{\sqrt{2}\,\pi\sigma^2\bar{C}N'^2}{2}$$

Solving

$$Z_{11} = \frac{\pi\sigma^2\bar{C}N'^2}{\sqrt{2}}$$

where

π = mathematical expression

σ = Collision diameter

$\bar{C}$ = Average molecular velocity $= \sqrt{\frac{8RT}{\pi M}}$

N' = Number of gases particles per unit volume

Putting the value of Average molecular velocity in collision frequency formula,

$$Z_{11} = \frac{\pi\sigma^2 N'^2}{\sqrt{2}} \times \sqrt{\frac{8RT}{\pi M}}$$

Solving : $\boxed{\frac{\sqrt{8}}{\sqrt{2}} = \sqrt{4}}$ $\boxed{\frac{\pi}{\sqrt{\pi}} = \sqrt{\pi}}$

$$Z_{11} = \frac{\sqrt{\pi}\,\sigma^2 N'^2}{1} \times \sqrt{\frac{4RT}{M}}$$

Solving : $\boxed{\sqrt{4} = 2}$

$$Z_{11} = \sqrt{\pi}\,\sigma^2 N'^2 \times 2 \times \sqrt{\frac{RT}{M}}$$

Solving : $\boxed{\sqrt{\pi} \times 2 = 3.54}$

$$Z_{11} = 3.54\,\sigma^2 N'^2 \sqrt{\frac{RT}{M}}$$

- Note: Collision frequency is inversely proportional to mass of the gas : As the weight increase, particle move slowly, hence less collision per unit time in per unit volume (i.e. Collision frequency).

Collision diameter

- Distance between the centre of two particle colliding is known as collision diameter.
- The collision diameter refers to the minimum distance between two objects that allows them to collide with each other. It is also known as the impact parameter or the closest approach distance.
- The collision diameter is an important factor in determining the outcome of a collision, such as the amount of energy transferred or the resulting damage.
- The collision diameter is an important parameter at the atomic level, where it has a significant impact on chemical reactions, phase transitions, and material properties.
- It is denoted by ssigma.

Mean free path: Definition

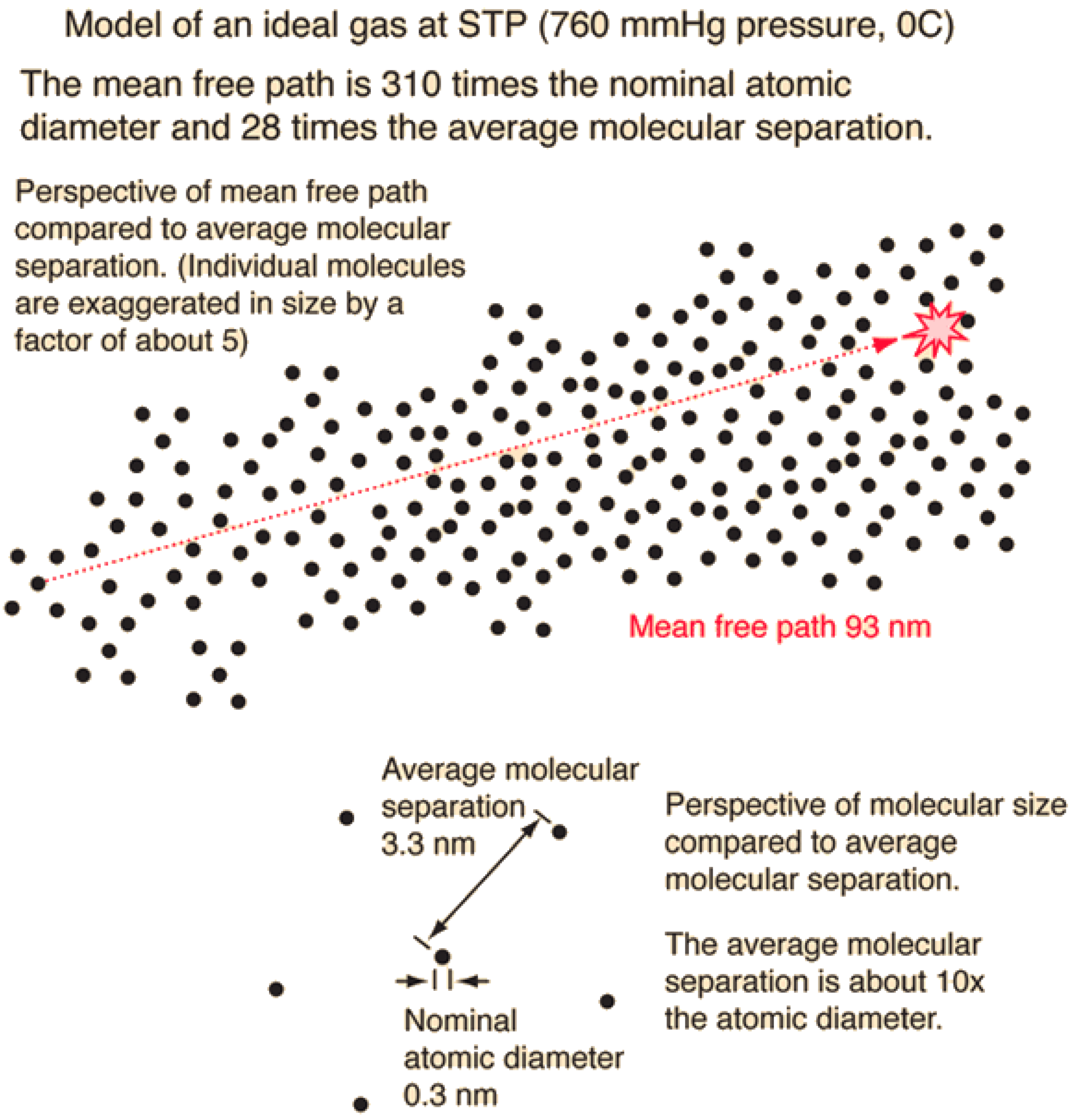
The mean free path is defined as the average distance covered by a gas molecule between two consecutive collisions with other gas molecules or with the walls of the container. It is a measure of the freedom of movement of the gas molecules and is inversely proportional to the gas pressure. In other words, the higher the pressure, the shorter the mean free path, and vice versa. The mean free path of a gas can be calculated using the formula:

mean free path = 1 / (collision frequency * collision cross-section)

where collision frequency is the number of collisions per unit time and collision cross-section is the effective area of the molecule that is involved in a collision.

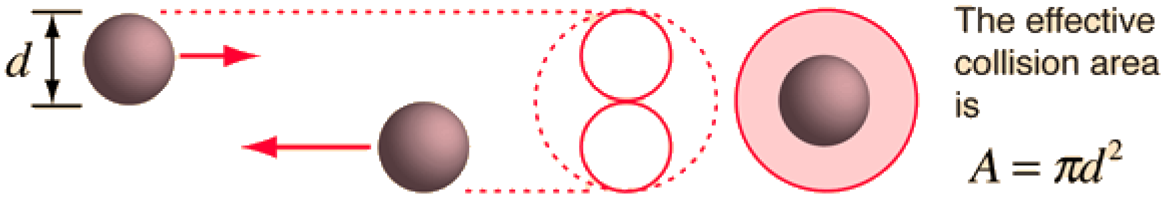
Mean Free Path: Perspective

You may be surprised by the length of the mean free path compared to the average molecular separation in an ideal gas. An atomic size of 0.3 nm was assumed to calculate the other distances.

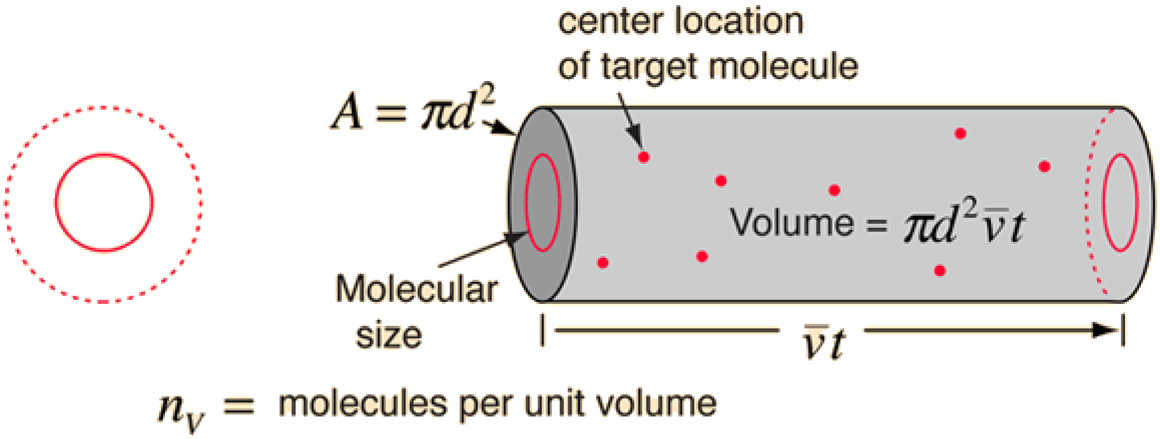

Model of an ideal gas at STP (760 mmHg pressure, 0C)
The mean free path is 310 times the nominal atomic diameter and 28 times the average molecular separation.
Perspective of mean free path compared to average molecular separation. (Individual molecules are exaggerated in size by a factor of about 5)
Mean free path 93 nm
Average molecular separation 3.3 nm
Nominal atomic diameter 0.3 nm
Perspective of molecular size compared to average molecular separation.
The average molecular separation is about 10x the atomic diameter.

Mean free path: Estimation

The mean free path or average distance between collisions for a gas molecule may be estimated from kinetic theory. Serway's approach is a good visualization - if the molecules have diameter d, then the effective cross-section for collision can be modeled by



using a circle of diameter 2d to represent a molecule's effective collision area while treating the "target" molecules as point masses. In time t, the circle would sweep out the volume shown and the number of collisions can be estimated from the number of gas molecules that were in that volume.


center location of target molecule
$A = \pi d^2$
Volume = $\pi d^2 \bar{v} t$
Molecular size
$\bar{v} t$
n_V = molecules per unit volume

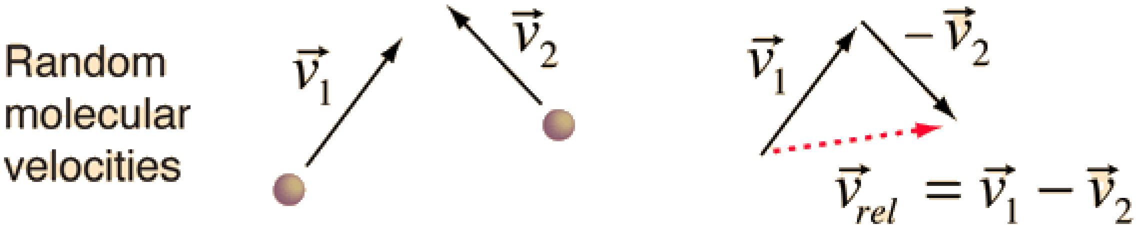
The mean free path could then be taken as the length of the path divided by the number of collisions.

$$\text{Mean free path estimate} = \frac{\overset{\text{Distance traveled}}{\bar{v}t}}{\underbrace{\pi d^2 \bar{v} t}_{\text{Volume of interaction}}\, \underset{\text{Number of molecules per unit volume}}{n_V}} = \overset{\text{Mean distance per collision}}{\frac{1}{\pi d^2 n_V}}$$

The problem with this expression is that the average molecular velocity is used, but the target molecules are also moving. The frequency of collisions depends upon the average relative velocity of the randomly moving molecules.

Calculate Relative velocity before refinement of mean free path

In order to calculate the mean free path for a molecule of a gas, it is necessary to assess the average relative velocity of the molecules involved rather than just the average velocity of any given molecule. The relative velocity of any two molecules can be expressed in terms of their vector velocities.


Random molecular velocities
$\vec{v}_1$
$\vec{v}_2$
$\vec{v}_1$
$-\vec{v}_2$
$\vec{v}_{rel} = \vec{v}_1 - \vec{v}_2$

The magnitude of the relative velocity can be expressed as the square root of the scalar product of the velocity with itself.

This expression can be expanded as follows.

$$v_{rel} = \sqrt{(\vec{v}_1 - \vec{v}_2)\cdot(\vec{v}_1 - \vec{v}_2)}$$

$$v_{rel} = \sqrt{\vec{v}_1 \cdot \vec{v}_1 - 2\vec{v}_1 \cdot \vec{v}_2 + \vec{v}_2 \cdot \vec{v}_2}$$

Taking the average of the terms leads to

$$\overline{v_{rel}} = \sqrt{\overline{\vec{v}_1 \cdot \vec{v}_1} - 2\underbrace{\overline{\vec{v}_1 \cdot \vec{v}_2}}_{=0} + \overline{\vec{v}_2 \cdot \vec{v}_2}}$$

$$\overline{v_{rel}} = \sqrt{\overline{v}_1^{\,2} + \overline{v}_2^{\,2}}$$

since $\vec{v}_1$ and $\vec{v}_2$ are random and uncorrelated.

Since the same average velocity would be associated with each molecule, this becomes

Average relative velocity $$\overline{v_{rel}} = \sqrt{2}\;\overline{v}$$

Mean free path: Refinement

The intuitive development of the mean free path expression suffers from a significant flaw - it assumes that the "target" molecules are at rest when in fact they have a high average velocity. What is needed is the average relative velocity, and the calculation of that velocity from the molecular speed distribution yields the result

Average relative velocity $$\overline{v_{rel}} = \sqrt{2}\;\overline{v}$$

which revises the expression for the effective volume swept out in time t

Effective volume of targets swept $$\pi d^2 \sqrt{2}\;\overline{v}t$$

The number of collisions is $\sqrt{2}$ times the number with stationary targets.

The resulting mean free path is

$$\lambda = \frac{1}{\sqrt{2}\,\pi d^2 n_V}$$

The number of molecules per unit volume can be determined from Avogadro's number and the ideal gas law, leading to

$$n_V = \frac{nN_A}{V} = \frac{nN_A}{\frac{nRT}{P}} = \frac{N_A P}{RT}$$

Mean free path

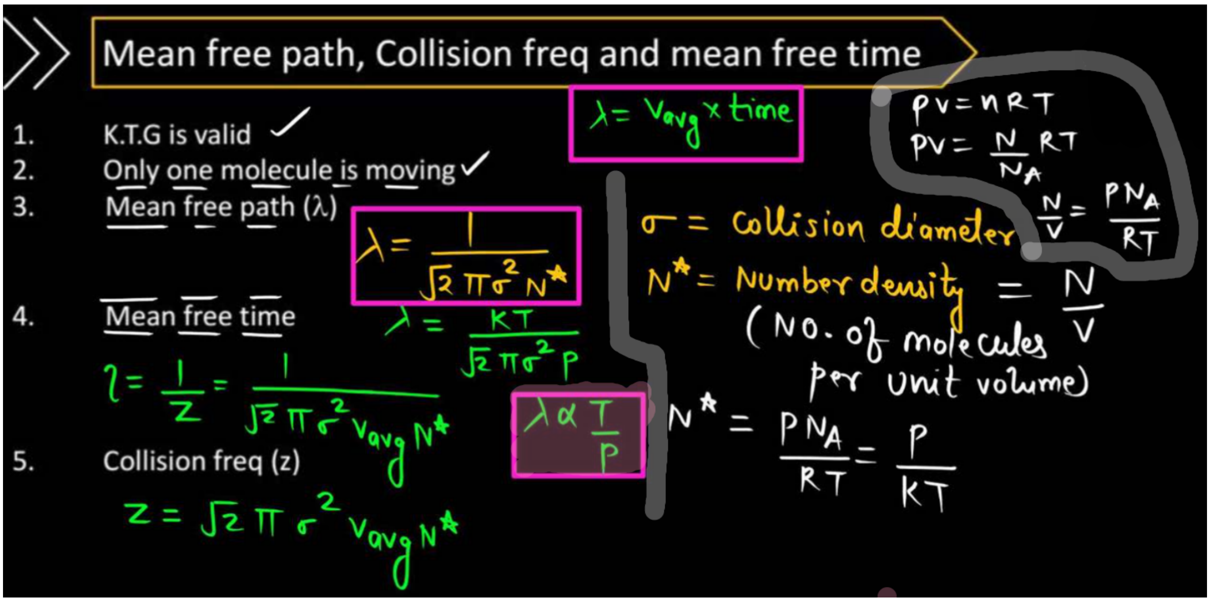
$$\lambda = \frac{RT}{\sqrt{2}\pi d^2 N_A P}$$

It should be noted that this expression for the mean free path of molecules treats them as hard spheres, whereas real molecules are not.

Mean free time:Definition

It refers to the average time interval between two consecutive interactions between particles in a system. In other words, it is the average time that a particle spends without colliding with another particle in a given system.

Summarize all three



Mean free path, Collision freq and mean free time

1. K.T.G is valid ✓
2. Only one molecule is moving ✓
3. Mean free path (λ)

$\boxed{\lambda = V_{avg} \times time}$

$\boxed{\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}}$

σ = Collision diameter

N^* = Number density $= \frac{N}{V}$

(No. of molecules per unit volume)

$PV = nRT$

$PV = \frac{N}{N_A} RT$

$\frac{N}{V} = \frac{PN_A}{RT}$

$N^* = \frac{PN_A}{RT} = \frac{P}{KT}$

$\lambda = \frac{KT}{\sqrt{2}\pi\sigma^2 P}$

$\boxed{\lambda \propto \frac{T}{P}}$

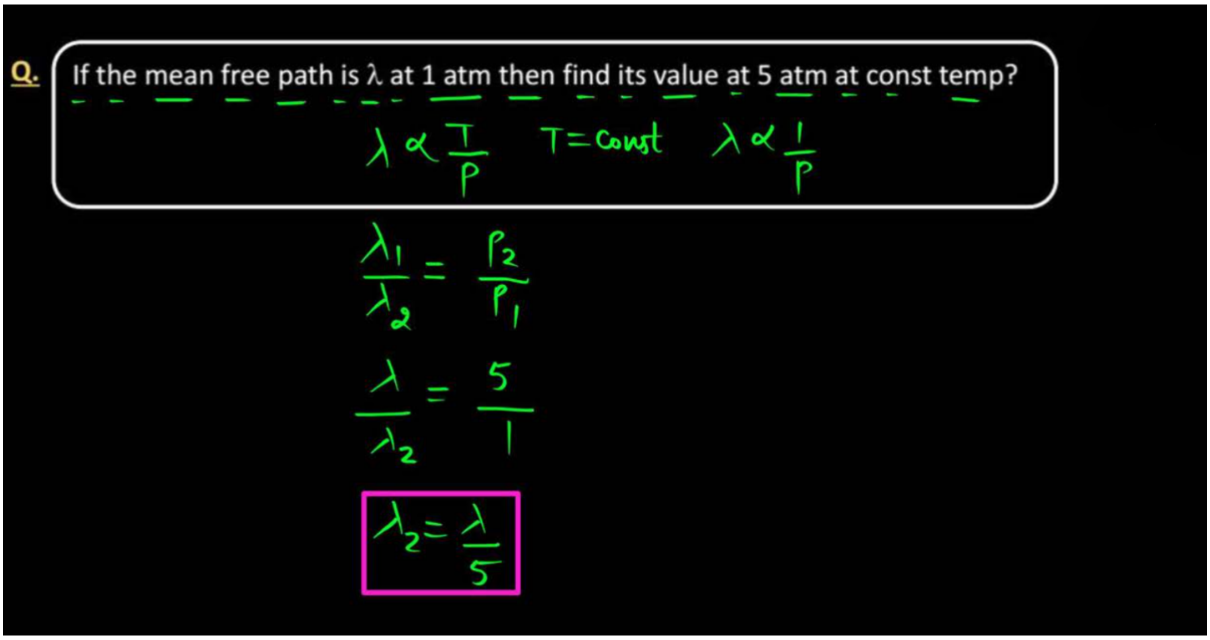
4. Mean free time

$\tau = \frac{1}{Z} = \frac{1}{\sqrt{2}\pi\sigma^2 V_{avg} N^*}$

5. Collision freq (z)

$Z = \sqrt{2}\pi\sigma^2 V_{avg} N^*$

Q&A



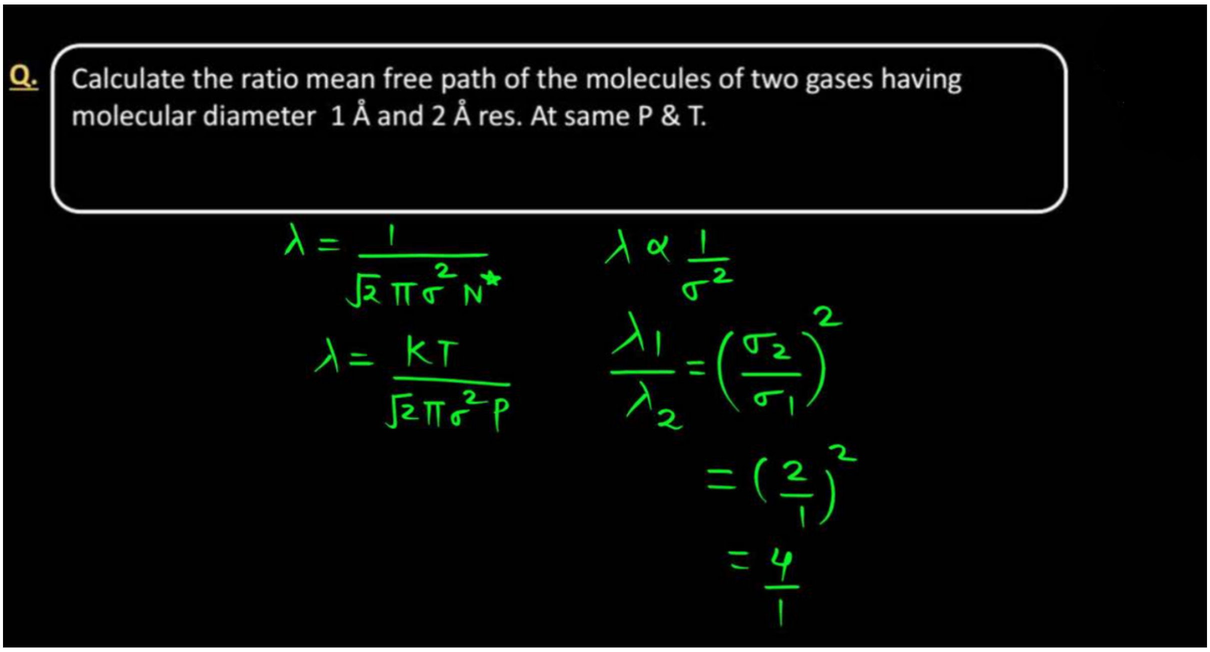
Q. If the mean free path is λ at 1 atm then find its value at 5 atm at const temp?

$\lambda \propto \frac{T}{P}$ $T = \text{Const}$ $\lambda \propto \frac{1}{P}$

$\frac{\lambda_1}{\lambda_2} = \frac{P_2}{P_1}$

$\frac{\lambda}{\lambda_2} = \frac{5}{1}$

$\boxed{\lambda_2 = \frac{\lambda}{5}}$



Q. Calculate the ratio mean free path of the molecules of two gases having molecular diameter 1 Å and 2 Å res. At same P & T.

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 N^*}$$

$$\lambda = \frac{KT}{\sqrt{2}\pi\sigma^2 P}$$

$$\lambda \propto \frac{1}{\sigma^2}$$

$$\frac{\lambda_1}{\lambda_2} = \left(\frac{\sigma_2}{\sigma_1}\right)^2$$

$$= \left(\frac{2}{1}\right)^2$$

$$= \frac{4}{1}$$